

## Friedel–Crafts polyalkylation of alkylbenzenes with dichloromethylvinylsilane

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### Abstract

The Friedel–Crafts alkylation of alkylbenzenes such as toluene, ethylbenzene, *n*-propylbenzene, *n*-butylbenzene, *o*-, *m*-, *p*-xylene, and mesitylene with dichloromethylvinylsilane in the presence of aluminum chloride catalyst has been studied under mild conditions. Alkylation with dichloromethylvinylsilane at room temperature gave peralkylated products in yields ranging from 25 to 63%, depending upon the number of substituents on the benzene ring. Less alkylated compounds were also obtained as minor products along with alkyl-reoriented products or transalkylated products. The alkylations of substituted benzenes such as chlorobenzene and anisole did not give the peralkylated products under the same conditions. The molecular structure of tris(dichloromethylsilylethyl)mesitylene has been determined by X-ray diffraction studies. The two chlorosilyl group containing substituents are arranged above the benzene plane and the other one below. Peralkylated compounds were methylated or reduced to the corresponding derivatives by reacting with methyl Grignard reagent and  $\text{LiAlH}_4$ . © 1997 Elsevier Science S.A.

### 1. Introduction

Hexaalkylbenzenes having small alkyl substituents such as hexamethylbenzene and hexaethylbenzene can be prepared in fair yields by the Friedel–Crafts type alkylation of benzene with methyl chloride and ethyl chloride or ethylene in the presence of Lewis acid catalyst [1]. However, propylation of benzene and propylbenzene with *n*-propyl chloride was reported to give a mixture of hexapropylbenzenes having *n*-propyl and *i*-propyl groups in low yield, probably due to the steric interactions of bulky propyl groups [2]. Although hexaalkylbenzenes have received much attention [3–18] because of the synthetic challenges for the sterically crowded molecular structures and their unique properties, the alkylation of benzene with chlorosilyl group containing alkyl halides or olefins to peralkylated products still remained unexplored. Hexaalkylbenzenes containing functional groups such as ethynyl or ferrocenyl

have been only prepared in multi-step syntheses and in poor yields [5–18]. The alkylation of substituted benzenes with alkenylsilanes has attracted little attention because of the low reactivity of vinylsilanes [19,20] and the difficulties of allylsilane syntheses [21,22]. Nametkin et al. first reported that the reaction of substituted benzenes with alkenylsilanes such as allylsilanes and vinylsilanes afforded mono- and di(silylethyl)benzene derivatives [23]. We also reported detailed information on the Friedel–Crafts type alkylation of substituted benzenes with allyldichlorosilane, including relative reaction rates and product isomer distribution [24]. In an extension of this study, we studied the polyalkylation of benzene with vinylchlorosilanes in the presence of aluminum chloride at room temperature and reported the new synthesis of silyl group containing hexaalkylated benzenes in one step [25].

In the present paper, we report syntheses of chlorosilyl group containing peralkylated benzenes by the Friedel–Crafts alkylation of various alkylbenzenes with dichloromethylvinylsilane and derivatization reactions using methyl Grignard reagent and  $\text{LiAlH}_4$ . The X-ray structure of 2,4,6-tris(dichloromethylsilylethyl)mesitylene is also reported.

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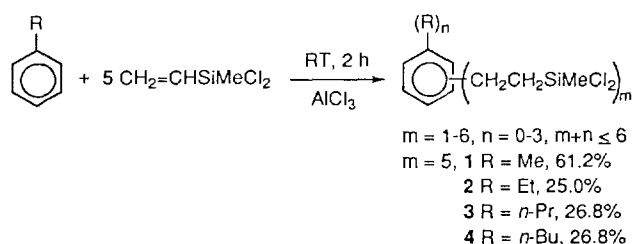
## 2. Results and discussion

### 2.1. Peralkylation of mono-alkylbenzenes

When one mole of toluene was reacted with five moles of dichloromethylvinylsilane in the presence of aluminum chloride at room temperature for 2 h, pentakis(dichloromethylsilylethyl)toluene **1** precipitated from the reaction solution as the major product in 61.2% yield. The yield was a little higher than hexakis(dichloromethylsilylethyl)benzene (56.0%) [25], supporting that electron-donating methyl substituent on phenyl ring activated the polyalkylation reaction. The remaining solution contained less alkylated products: (dichloromethylsilylethyl)toluene (1.5%), bis(dichloromethylsilylethyl)toluene (1.9%), tris(dichloromethylsilylethyl)toluene (6.2%), and tetrakis(dichloromethylsilylethyl)toluene (11.6%) based on toluene used.

Peralkylated product **1** was further recrystallized from THF as colorless needle-type crystals and the structure was determined by spectroscopic analysis. In  $^1\text{H}$  NMR spectrum, Si–Me protons revealed two peaks at 0.84 and 0.86 ppm in 2:3 ratio, indicating two kinds of Si–Me groups. This might be attributed to either the up and down alternation of five dichloromethylsilyl ethyl groups around benzene ring [25] or the two meta-substituted silyl groups and the other three silyl groups at *para*- and *ortho*-positions. Based on the analogy to the hexakis(dichloromethylsilylethyl)benzene, two signals at 1.27–1.34 and 2.73–2.83 ppm can be easily assigned to the consecutive  $\text{CH}_2$  protons next to the silyl group and the peak at 2.27 ppm to the phenyl– $\text{CH}_3$  protons. No signals appeared in the benzene region because of the all six substitutions.  $^{13}\text{C}$  NMR spectrum also showed similar features to those of hexakis(dichloromethylsilylethyl)benzene [25]. Two peaks at 5.76 and 5.82 ppm corresponded to the two kinds of Si–Me carbon peak, but  $\text{CH}_2$ –Si carbons revealed as one peak at 16.08 ppm. On the other hand, three peaks at 23.27, 23.46, and 25.03 ppm showed three kinds of  $\text{CH}_2$ –phenyl carbons probably due to the three benzylic carbons at *o*-, *m*-, and *p*-positions. The four peaks at 133.23, 137.17, 137.41, and 139.01 corresponded to the four different benzene carbons.

The compound **1'**, methylated product of **1** using methyl Grignard reagent, showed similar spectroscopic features to those of **1**: four signals appeared at 0.10, 0.11, 0.74–0.80, and 2.51–2.58 ppm were due to the two kinds of Si–Me and two  $\text{CH}_2$  protons of the five silylethyl substituents, and the phenyl– $\text{CH}_3$  protons was observed at 2.20 ppm. In  $^{13}\text{C}$  NMR spectrum, however, peaks were more complicated: All the Si–Me carbons (at –1.74, –1.59, and –1.54 ppm), Si– $\text{CH}_2$  carbons (at 18.29, 20.08, and 20.18 ppm) and  $\text{CH}_2$ –phenyl carbons (at 23.19, 23.24 and 23.79 ppm) gave three peaks probably due to the three substituents at *o*-,



Scheme 1.

*m*-, and *p*-positions. Four peaks at 130.68, 137.74, 137.99, and 139.22 ppm in the benzene region corresponded to the four kinds of phenyl carbons. The identification of less alkylated products and product distribution were performed based on GC/MS data of the methylated products because they were more stable toward the atmosphere and lower the molecular mass.

The peralkylation of mono-alkylbenzenes having higher alkyl groups such as ethyl, *n*-propyl, and *n*-butyl with dichloromethylvinylsilane also gave the peralkylated products, but the yields were about 25% as shown in Scheme 1.

When ethylbenzene was reacted with five moles of dichloromethylvinylsilane under the same reaction conditions as described for **1**, white solids precipitated from the reaction solution, which could be recrystallized from THF solution as colorless needle-type crystals. Spectroscopic analysis after methylation using methyl Grignard reagent showed that these solids were composed of two kinds of peralkylated products, pentakis(dichloromethylsilylethyl)ethylbenzene **2** (25.0%) and tetrakis(dichloromethylsilylethyl)diethylbenzene (3.9%) in about 6:1 ratio. The remaining solution contained less alkylated products: bis(dichloromethylsilylethyl)ethylbenzene (1.0%), tris(dichloromethylsilylethyl)ethylbenzene (4.4%), and tetrakis(dichloromethylsilylethyl)ethylbenzene (8.7%) as well as transalkylated products of bis(dichloromethylsilylethyl)diethylbenzene (1.8%), tris(dichloromethylsilylethyl)diethylbenzene (10.7%), tetrakis(dichloromethylsilylethyl)diethylbenzene (7.4%), tris(dichloromethylsilylethyl)benzene (4.8%), tetrakis(dichloromethylsilylethyl)benzenes (6.6%), and pentakis(dichloromethylsilylethyl)benzene (7.9%), along with trace amount of bis(dichloromethylsilylethyl)benzenes, hexakis(dichloromethylsilylethyl)benzenes, and bis(dichloromethylsilylethyl)triethylbenzenes according to GLC area percent.

It is of interest that higher alkyl substituted benzenes showed different behavior in the peralkylation with dichloromethylvinylsilane. Transalkylated products were well predictable because Anschutz first reported the disproportionation of alkylbenzenes in the presence of Lewis acid as early as in 1886 [26,27]. When toluene was heated with aluminum chloride at reflux, it was found that toluene was converted into a mixture of

Table 1  
Polyalkylation of alkylbenzenes

R	Product yields (%)	Less alkylated products ( $n = 1$ )				Transalkylated products <sup>a</sup> ( $n = 0$ or $n = 2$ )
		$m = 1$	$m = 2$	$m = 3$	$m = 4$	
Me	61.2 (1)	1.5	1.9	6.2	11.6	
Et	25.0 (2)	0	1.0	4.4	8.7	bis(sil)diethylbenzene (1.8) tris(sil)diethylbenzene (10.7) tetrakis(sil)diethylbenzene (11.3) bis(sil)diethylbenzene (1.8) tris(sil)benzene (4.8) tetrakis(sil)benzene (6.6) pentakis(sil)benzene (7.9) bis(sil)benzene (trace) hexakis(sil)benzene (trace) bis(sil)benzene (trace)
<i>n</i> -Pr	26.0 (3)	3.0	8.1	9.5	12.4	tetrakis(sil)di- <i>n</i> -propylbenzene (9.0) (sil)benzene (1.8) bis(sil)benzene (2.0)
<i>n</i> -Bu	26.8 (4)	6.8	10.1	11.1	13.1	tetrakis(sil)di- <i>n</i> -butylbenzene (8.2) (sil)benzene (1.1) bis(sil)benzene (1.6)

<sup>a</sup>sil represents dichloromethylsilylethyl group.

benzene and xylenes, said to be mainly the *m*- and *p*-isomers. Similarly, ethylbenzene gave benzene and a mixture of *m*- and *p*-diethylbenzene. In 1935, Baddeley and Kenner presented a convincing evidence that the products obtained from the disproportionation of *p*-di-*n*-propylbenzene in the presence of aluminum chloride were *n*-propylbenzene, *m*-di-*n*-propylbenzene, and 1,3,5-tris-*n*-propylbenzene [27,28]. Thus, it may be concluded that the transalkylation of ethylbenzene to the mixture of ethylbenzene, benzene and diethylbenzene, followed by the polyalkylation with dichloromethylvinylsilane attributed to the many byproducts. This indicates that the transalkylation of ethylbenzene was responsible for the significantly lower yield (25.0%) of **2** in comparison with those of hexakis(dichloromethylsilylethyl)benzene [25] or **1**. All the less alkylated and transalkylated products were methylated using methyl Grignard reagent and the products distribution was determined based upon the GC/MS area percents of the methylated products.

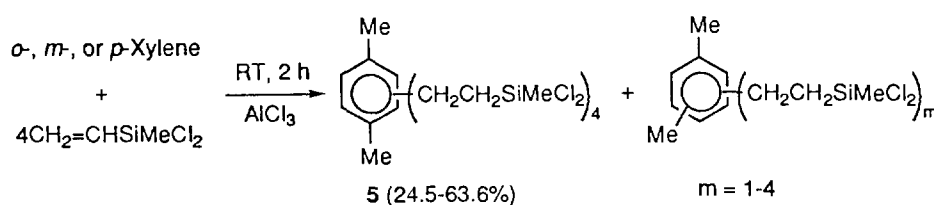
Peralkylation of *n*-propylbenzene and *n*-butylbenzene showed similar results to those of ethylbenzene. The peralkylated products **3** and **4** were converted to the

methylated compounds using methyl Grignard reagent for satisfactory characterization by elemental analysis and NMR spectroscopy. The results from the alkylation of alkylbenzenes along with the products distribution of transalkylated compounds are summarized in Table 1.

## 2.2. Peralkylation of higher methylbenzenes

When each *o*-, *m*-, or *p*-xylene was reacted with four moles of dichloromethylvinylsilane under the reaction conditions described above, peralkylated xylenes were formed as a mixture of isomers such as tetrakis(dichloromethylsilylethyl)-*o*-xylene or tetrakis(dichloromethylsilylethyl)-*m*-xylene and tetrakis(dichloromethylsilylethyl)-*p*-xylene **5** as shown in Scheme 2.

It has been demonstrated by several investigators that methylarenes undergo reorientation without any observable transalkylation. Baddeley et al. reported that a mixture of *p*-xylene and aluminum bromide kept at room temperature for 1 day gave no change in the hydrocarbon, but in the presence of hydrogen bromide, reorientation occurred to produce a mixture of the three xylene isomers (in a ratio of ca. 67:27:2, *m/p/o*), with



Scheme 2.

no appreciable formation of transalkylation products [27,29]. These reports well correspond to our present results.

Because of the high structural symmetry **5** was easily separated and purified by recrystallization from THF solution. The high symmetry of **5** was well revealed in NMR spectroscopy: in  $^1\text{H}$  NMR spectrum, three signals were observed at 0.88, 1.28–1.34, and 2.80–2.85 ppm due to the Si–Me and two  $\text{CH}_2$  protons and one peak at 2.29 ppm due to the phenyl– $\text{CH}_3$  protons. No signals appeared in the benzene region indicating the peralkylation.  $^{13}\text{C}$  NMR spectrum, however, showed three signals at 5.11, 15.26, and 22.71 ppm because of the Si–Me two  $\text{CH}_2$  carbons. One peak appeared at 22.71 ppm due to the  $\text{CH}_3$ –phenyl and two signals at 131.54 and 137.55 ppm due to two kinds of benzene carbons. The less alkylated products, mono- to tris-alkylated compounds were also formed along with many isomers due to the reorientation of methyl group. Other peralkylated products and less alkylated products were identified using GC/MS after methylation using methyl Grignard reagent. The yields of peralkylated and less alkylated products including the number of isomers are summarized in Table 2.

Peralkylation of mesitylene with dichloromethylvinylsilane gave only reoriented products but no transalkylated products. We, however, found out that the undesirable isomerization of 2,4,6-tris (dichloromethylsilyl)ethyl)mesitylene **6** to 3,5,6- or 4,5,6-isomers could be avoided by carrying out the reaction in hexane solution at room temperature for 12 h. Thus, **6** precipitated from the reaction mixture as the major product in 38% yield and was recrystallized from THF solution.  $^1\text{H}$  NMR spectrum revealed its high structural symmetry and no signal was appeared in the benzene region. Four signals at 0.88, 1.27–1.33, 2.85–2.91, and 2.31 ppm were observed due to the Si–Me and two  $\text{CH}_2$  protons, and phenyl– $\text{CH}_3$  protons, respectively.  $^{13}\text{C}$  NMR spectrum showed four signals at 5.11, 15.49, 21.62, 23.08 ppm due to the Si–Me and two  $\text{CH}_2$  protons, and phenyl– $\text{CH}_3$  carbons and two signals at 131.18 and 138.17 ppm due to two kinds of benzene carbons, which were well agreeable with the  $^1\text{H}$  NMR spectrum. The remaining solution contained less alkylated products, one mono- and one bis-alkylated mesitylenes (**6-2** and **6-1**) without any reoriented products in 7.0% and 37.0% yield, respectively, which were separated in pure form by a recrystallization or vacuum distillation. Subsequent NMR spectral analyses allowed the assignments of their structures based on the chemical shift and the integration ratio of peaks of two  $\text{CH}_2$  protons and benzene protons in their  $^1\text{H}$  NMR spectra.

The chloro-derivatives **6**, **6-1**, and **6-2** were converted to the methylated compounds by treating with methyl Grignard reagent and **6** was also reduced using  $\text{LiAlH}_4$  to give the corresponding hydrido-derivatives. These derivatives were obtained in good to excellent yields after purification by a recrystallization or vacuum distillation. All new derivatives were satisfactorily characterized by elemental analysis and NMR spectroscopy.

The Friedel–Crafts type polyalkylations of alkyl-substituted benzenes with dichloromethylvinylsilane become easier and faster as the number of electron-donating methyl groups on the phenyl group increases. This is consistent with the fact that the alkylation occurs in the fashion of electrophilic substitution. The tendency of starting methylbenzenes to form reoriented products also increases in the same order—from toluene to mesitylene.

The alkylation of benzenes having electron withdrawing groups, such as chlorobenzene and anisole, with dichloromethylvinylsilane gave only mono-, bis- and tris-alkylated derivatives<sup>1</sup>, but no peralkylated products were obtained even upon heating of the reaction mixtures for a long time. It might be due to the deactivation effect by the electron-withdrawing substituents and the complexation between  $\text{AlCl}_3$  catalyst and the lone pair electrons on the substituents.

The Friedel–Crafts type polyalkylations of alkyl-substituted benzenes with dichloromethylvinylsilane become easier and faster as the number of electron-donating methyl groups on the phenyl group increases. This is consistent with the fact that the alkylation occurs in the fashion of electrophilic substitution. The tendency of starting methylbenzenes to form reoriented products also increases in the same order—from toluene to mesitylene.

### 2.3. X-ray crystallographic analysis of **6**

Single crystal of **6** suitable for X-ray analysis was grown by slow evaporation of a saturated hexane solution and the X-ray structure was shown in Fig. 1. Crystallographic data, bond lengths and angles for **6** were shown in Tables 3 and 4.

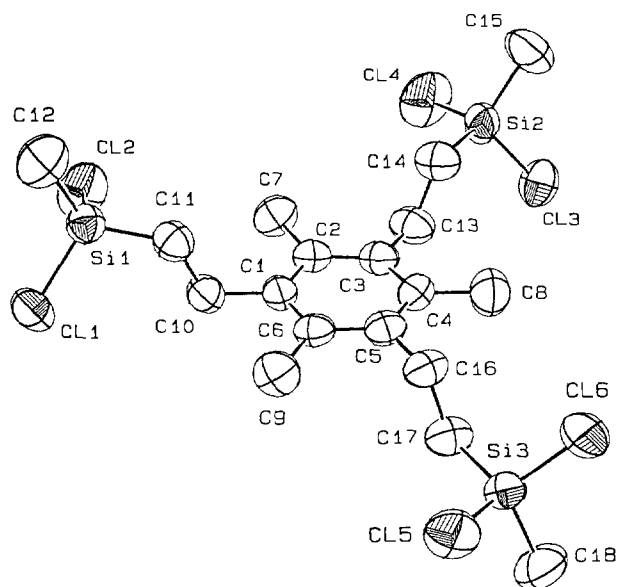
According to the crystal structural data, two of silyl containing substituents of **6** are arranged above the benzene ring and one group is, minimizing the steric interactions between the bulky substituents as revealed in those of hexasubstituted benzenes [30–33]. The average value of the ring-carbon bond distances ( $C_{ar}-C_{ar}$ ), 1.403 Å, is slightly longer than in benzene (1.39 Å) but the six benzene carbons are nearly coplanar. The average  $C_{ar}-C_{ar}-C_{ar}$  bond angles and  $\text{CH}_2-\text{CH}_2-\text{Si}$  bond angles are 119.9° and 115.4°, respectively. The

Table 2  
Peralkylation of xylenes

Xylene	Product yields (%)			
	Peralkylated products <sup>a</sup> (% of <b>5</b> )	Less alkylated products (isomers)		
		$m = 1$	$m = 2$	$m = 3$
<i>o</i> -xylene	75.0 (29.1)	1.2 (1)	4.7 (4)	9.3 (4)
<i>m</i> -xylene	29.1 (24.5)	3.5 (1)	11.3 (4)	39.1 (4)
<i>p</i> -xylene	75.8 (63.6)	0.8 (1)	3.8 (5)	8.4 (4)

<sup>a</sup>The isomeric mixture of peralkylated products.

<sup>1</sup>I.N. Jung, unpublished results.

Fig. 1. Molecular structure of **6** in the crystal.Table 3  
Crystallographic details for **6**

Formula	$C_{18}H_{30}Cl_6Si_3$
<i>M</i>	543.39
Temperature, K	293 (2)
Cryst size, mm	0.33 × 0.33 × 0.40
Cryst system	Triclinic
Space group	PT (No.2)
<i>a</i> , Å	10.015 (3)
<i>b</i> , Å	11.568 (2)
<i>c</i> , Å	12.931 (2)
$\alpha$ , deg	84.050 (14)
$\beta$ , deg	68.43 (2)
$\gamma$ , deg	77.60 (2)
<i>V</i> , Å <sup>3</sup>	1360.2 (5)
<i>z</i>	2
<i>d</i> <sub>calc</sub> , Mg/m <sup>3</sup>	1.327
Absorption coefficient, mm <sup>-1</sup>	0.768
<i>F</i> (000)	564
Scan type	$\theta$
$\theta$ Range, deg	1.80–24.95
Index ranges	0 < - <i>h</i> < -11, -13 < - <i>k</i> < -13, -14 < - <i>l</i> < 15
Reflections collected	2715
Independent reflections { <i>I</i> > 2 $\sigma$ ( <i>I</i> )}	2547 [R (int) = 0.0224]
Refinement method	full-matrix least-squares on <i>F</i> <sup>2</sup>
Data to parameter ratio	2547/244
Final <i>R</i> indices { <i>I</i> > 2 $\sigma$ ( <i>I</i> )}	<i>R</i> <sub>1</sub> = 0.0740, <i>wR</i> <sub>2</sub> = 0.1992
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.0771, <i>wR</i> <sub>2</sub> = 0.2032
GOF on <i>F</i> <sup>2</sup>	0.990
Largest diff. peak and hole, eÅ <sup>-3</sup>	0.684, -0.303

$$R_1 = \frac{\sum |F_o| - |F_c|}{\sum |F_o|}, \quad wR_2 = \frac{\{\sum [w(F_o^2 - F_c^2)^2]\}}{\{\sum [w(F_o^4)]\}}^{1/2},$$

$$w = 1 / \{\sigma^2(F_o^2) + (0.1419P)^2 + 1.86P\} \quad \text{where } P = \{\text{Max}(F_o^2, 0) + 2F_c^2\} / 3.$$

average bond length between silicon and carbon atom for Si-CH<sub>3</sub> (1.941 Å) is well comparable with the values of 1.89 Å and 1.87 Å reported for Si-(CH<sub>3</sub>)<sub>4</sub>

Table 4  
Bond lengths and angles for **6**

Si(1)-C(11)	1.839(7)	Si(1)-C(12)	1.897(6)
Si(1)-Cl(2)	2.028(3)	Si(1)-Cl(1)	2.047(3)
Si(2)-C(14)	1.831(8)	Si(2)-Cl(4)	1.980(4)
Si(2)-C(15)	1.995(6)	Si(2)-Cl(3)	1.998(4)
Si(3)-C(17)	1.836(7)	Si(3)-Cl(18)	1.930(5)
Si(3)-Cl(6)	1.988(4)	Si(3)-Cl(5)	2.026(4)
C(1)-C(2)	1.398(9)	C(1)-C(6)	1.404(9)
C(1)-C(10)	1.520(9)	C(2)-C(3)	1.412(9)
C(2)-C(7)	1.510(9)	C(3)-C(4)	1.392(9)
C(4)-C(8)	1.528(10)	C(5)-C(6)	1.411(9)
C(5)-C(16)	1.500(9)	C(6)-C(9)	1.506(10)
C(10)-C(11)	1.539(9)	C(13)-C(14)	1.528(10)
C(16)-C(17)	1.544(10)		
C(11)-Si-(1)-C(12)	133.6(3)	C(11)-Si-(1)-Cl(2)	108.7(3)
C(12)-Si-(1)-C(2)	110.2(2)	C(11)-Si-(1)-Cl(1)	109.7(3)
C(12)-Si-(1)-C(1)	107.9(2)	Cl(2)-Si-(1)-Cl(1)	106.4(2)
C(14)-Si-(2)-C(4)	110.0(3)	C(14)-Si-(2)-C(15)	107.9(3)
C(4)-Si-(2)-C(15)	111.9(3)	C(14)-Si-(2)-Cl(3)	110.2(3)
C(4)-Si-(2)-C(3)	107.0(2)	C(15)-Si-(2)-Cl(3)	109.9(2)
C(17)-Si-(3)-C(18)	112.8(3)	C(17)-Si-(3)-Cl(6)	110.5(3)
C(18)-Si-(3)-C(6)	110.7(2)	C(17)-Si-(3)-Cl(5)	109.4(3)
C(18)-Si-(3)-C(5)	106.2(2)	Cl(6)-Si-(3)-Cl(5)	107.0(2)
C(2)-C-(1)-C(6)	120.8(6)	C(2)-C-(1)-C(2)	118.9(6)
C(6)-C-(1)-C(10)	120.2(6)	C(1)-C-(2)-C(3)	119.4(6)
C(1)-C-(2)-C(7)	120.5(6)	C(3)-C-(2)-C(7)	120.1(6)
C(4)-C-(3)-C(2)	119.5(6)	C(4)-C-(3)-C(13)	120.5(6)
C(2)-C-(3)-C(13)	120.0(6)	C(5)-C-(4)-C(3)	121.2(6)
C(5)-C-(4)-C(8)	118.3(6)	C(3)-C-(4)-C(8)	120.5(6)
C(4)-C-(5)-C(6)	119.2(6)	C(4)-C-(5)-C(16)	120.9(6)
C(6)-C-(5)-C(16)	119.8(6)	C(1)-C-(6)-C(5)	119.5(6)
C(1)-C-(6)-C(9)	120.3(6)	C(5)-C-(6)-C(9)	120.2(6)
C(1)-C-(10)-C(11)	112.4(6)	C(10)-C-(11)-Si(1)	115.3(5)
C(14)-C-(13)-C(3)	112.4(6)	C(13)-C-(14)-Si(2)	115.5(5)
C(5)-C-(16)-C(17)	113.0(6)	C(16)-C-(17)-Si(3)	115.8(5)

[34] and Ph-Si-(CH<sub>3</sub>)<sub>3</sub> [35] and the average bond length between silicon and carbon for Si-CH<sub>2</sub>CH<sub>2</sub> is 1.685 Å. The bond distance for Si-Cl (2.01 Å) conforms with the reported value of 2.05 Å (Me<sub>3</sub>Si-Cl) [34]. The average bond length between carbon and carbon atom for Car-CH<sub>3</sub> (1.515 Å) and the average bond angle for Car-Car-CH<sub>3</sub> (120.3°) are well comparable with the values of 1.54 Å and 120° reported for C-C and C-C-C [36].

### 3. Experimental

#### 3.1. General comments

All reactions were carried out under an atmosphere of prepurified nitrogen. All glassware was flame-dried or oven-dried prior to use. Solvents were purified by standard procedures. Dichloromethylvinylsilane was distilled immediately before use. Anhydrous aluminum chloride was purchased from Aldrich Chemical and used without further purification. Toluene, ethylben-

zene, *n*-propylbenzene, *n*-butylbenzene, *o*-, *m*-, *p*-xylenes and mesitylene were purchased from Oriental Chemical or Aldrich Chemical and used without further purification. All air-sensitive liquids and dried solvents were transferred by standard syringe or double-tipped-needle techniques. Reaction products were analyzed by GLC using capillary column (SE-30, 30 m) or a packed column (10% OV-101 on 80–100 mesh Chromosorb W/AW, 1/8 in.  $\times$  1.5 m) on a Varian 3300 gas chromatograph equipped with a flame ionization detector or a thermal conductivity detector. The samples for characterization were purified by a preparative GLC using a Varian Aerograph Series 1400 gas chromatograph with a thermal conductivity detector and a 2 m  $\times$  1/8 in. stainless steel column packed with 20% OV-101 on 80–100 mesh Chromosorb P/AW. Mass spectra were obtained using a Hewlett-Packard 5890 Series II gas chromatograph equipped with a 5972 mass selective detector. High resolution mass spectra (70 eV, EI) were performed by the Chemistry Instrumentation Center of University of Wisconsin, WI, USA. NMR spectra were recorded on a Varian spectrometer using samples in CDCl<sub>3</sub> solution: <sup>1</sup>H NMR spectra at 300 MHz, <sup>13</sup>C NMR at 75.4 MHz. Melting points were obtained with a Melt Temp II. Elemental analyses were performed by the Advanced Analysis Center of the Korea Institute of Science and Technology, Seoul, Korea.

### 3.2. Synthesis of peralkylated benzene derivatives

#### 3.2.1. Pentakis(dichloromethylsilylethyl)toluene (1)

To a suspension of 0.12 g (0.90 mmol) of aluminum chloride in 0.59 g (9.35 mmol) of toluene, 6.59 g (46.75 mmol) of dichloromethylvinylsilane was added at the rate of 0.2 cc/min using a syringe pump, at room temperature with stirring. A moderate exothermic reaction was observed. After stirring for 2 h, a large amount of solid was formed which made stirring impossible. Freshly distilled 15 ml of hexane and 0.29 g (4.96 mmol) of NaCl powder were added to the reaction mixture and the mixture was then warmed up to 70°C to deactivate the Aluminum chloride for 1 h. Solid product and AlCl<sub>3</sub>–NaCl complex insoluble in hexane were filtered from mother liquid. Solids were washed twice with hexane, dissolved in dried THF, and the solid of AlCl<sub>3</sub>–NaCl complex was filtered off. Evaporation of THF from the solution yielded a yellowish white powder of pentakis(dichloromethylsilylethyl)toluene **1** and recrystallization from THF gave 4.15 g (61.2%) of **1** as colorless needles, mp 254–256°C. HRMS (*m/e*): Calc. for C<sub>22</sub>H<sub>38</sub>Si<sub>5</sub>C<sub>110</sub> (M<sup>+</sup>), 791.8705; Found, 791.8705. <sup>1</sup>H NMR  $\delta$  0.84 (s, 6H, CH<sub>3</sub>), 0.86 (s, 9H, CH<sub>3</sub>), 1.27–1.34 (m, 10H, CH<sub>2</sub>), 2.27 (s, 3H, CH<sub>3</sub>), 2.73–2.81 (m, 10H, CH<sub>2</sub>). <sup>13</sup>C NMR  $\delta$  5.76, 5.82 (CH<sub>3</sub>), 16.08 (CH<sub>2</sub>), 22.88 (CH<sub>3</sub>), 23.27, 23.46, 25.03 (CH<sub>2</sub>), 133.23, 137.17, 137.41, 139.01 (phenyl–C).

#### 3.2.2. Pentakis(trimethylsilylethyl)toluene (1')

To a solution of 0.47 g (0.59 mmol) of **1** and 30 ml of THF, 2.0 ml of 3 M methylmagnesium chloride in THF (6.00 mmol) was added dropwise with stirring. A slight exothermic reaction was observed. After the addition was completed, the mixture was stirred at room temperature for 2 h. Subsequently, it was poured into a saturated aqueous solution of NH<sub>4</sub>Cl. The aqueous layer was extracted with diethyl ether, and the combined organic layers were washed twice with 50 ml of water and 20 ml of saturated NaCl and were dried over anhydrous MgSO<sub>4</sub>. Rotary evaporation of volatiles left 0.23 g of **1'** as a yellow semisolid in, 65.1% yield, which was further purified using preparative GLC for characterization. Anal. Calc. for C<sub>32</sub>H<sub>68</sub>Si<sub>5</sub>: C, 64.78; H, 11.55. Found: C, 64.9; H, 11.7. <sup>1</sup>H NMR  $\delta$  0.10 (s, 27H, CH<sub>3</sub>), 0.11 (s, 18H, CH<sub>3</sub>), 0.74–0.80 (m, 10H, CH<sub>2</sub>), 2.20 (s, 3H, CH<sub>3</sub>), 2.51–2.58 (m, 10H, CH<sub>2</sub>). <sup>13</sup>C NMR  $\delta$  –1.74, –1.59 (CH<sub>3</sub>), 15.10 (CH<sub>3</sub>), 18.29, 20.08, 20.18 (CH<sub>2</sub>), 23.19, 23.24, 23.79 (CH<sub>2</sub>), 130.68, 137.74, 137.99, 139.22 (phenyl–C).

#### 3.2.3. Pentakis(dichloromethylsilylethyl)ethylbenzene (2)

Reaction of 0.87 g (8.20 mmol) of ethylbenzene with 5.76 g (41.0 mmol) of dichloromethylvinylsilane and 0.47 g (3.52 mmol) of aluminum chloride using the procedure described for **1** gave 1.66 g (25.0%) of **2** as a white powder, mp 185–188°C. HRMS (*m/e*): Calc. for C<sub>23</sub>H<sub>40</sub>Si<sub>5</sub>C<sub>110</sub> (M<sup>+</sup>), 805.8862; Found, 805.8862. <sup>1</sup>H NMR  $\delta$  0.87 (s, 15H, CH<sub>3</sub>), 1.20 (t, *J* = 7 Hz, 3H, CH<sub>3</sub>), 1.29–1.36 (m, 10H, CH<sub>2</sub>), 2.59 (q, *J* = 7 Hz, 2H, CH<sub>2</sub>), 2.71 = 2.77 (m, 10H, CH<sub>2</sub>). <sup>13</sup>C NMR  $\delta$  5.00, 5.31 (CH<sub>3</sub>), 15.63 (CH<sub>3</sub>), 21.87, 22.05, 22.34 (CH<sub>2</sub>), 22.88 (CH<sub>3</sub>), 23.94, 24.35, 24.48, 25.49 (CH<sub>2</sub>), 136.70, 137.05, 137.74 (phenyl–C).

#### 3.2.4. Pentakis(trimethylsilylethyl)ethylbenzene (2')

Reaction of 0.43 g (0.53 mmol) of **2** with 3 ml of 3 M of methylmagnesium chloride in THF (9.00 mmol) using the procedure described for **1'** gave a yellow semisolid, which was dissolved in 1 ml of hexane and subjected to column chromatography (silica gel, hexane) to give **2'** as a white powder (0.30 g, 93.0%). Anal. Calc. for C<sub>33</sub>H<sub>70</sub>Si<sub>5</sub>: C, 65.26; H, 11.62. Found: C, 65.2; H, 11.7. <sup>1</sup>H NMR  $\delta$  0.09 (s, 45H, CH<sub>3</sub>), 0.75–0.80 (m, 10H, CH<sub>2</sub>), 1.19 (t, *J* = 7 Hz, 3H, CH<sub>3</sub>), 2.49–2.55 (m, 12H, CH<sub>2</sub>CH<sub>3</sub>, CH<sub>2</sub>). <sup>13</sup>C NMR  $\delta$  –1.83, –1.58 (CH<sub>3</sub>), 15.54 (CH<sub>2</sub>), 19.52, 20.04, 20.15, 22.08, 23.05, 23.13 (CH<sub>2</sub>), 136.65, 138.07, 138.29, 138.68 (phenyl–C).

#### 3.2.5. Pentakis(dichloromethylsilylethyl)-*n*-propylbenzene (3)

Reaction of 0.87 g (7.17 mmol) of *n*-propylbenzene with 5.06 g (35.9 mmol) of dichloromethylvinylsilane and 0.47 g (3.52 mmol) of aluminum chloride using the

procedure described for **1** gave 1.59 g (26.8%) of **3** as a white powder, mp 201–206°C.  $^1\text{H}$  NMR  $\delta$  0.87 (s, 45H,  $\text{CH}_3$ ), 1.01 (t,  $J = 7$  Hz, 3H,  $\text{CH}_3$ ), 1.30–1.37 (m, 10H,  $\text{CH}_2$ ), 1.49–1.54 (m, 2H,  $\text{CH}_2$ ), 2.49 (t,  $J = 8$  Hz, 2H,  $\text{CH}_2$ ), 2.71–2.79 (m, 10H,  $\text{CH}_2$ ).  $^{13}\text{C}$  NMR  $\delta$  4.80, 4.88, 4.97 ( $\text{CH}_3$ ), 14.78 ( $\text{CH}_3$ ), 21.73, 22.00, 22.29, 23.93, 24.14, 24.34, 24.47, 31.88 ( $\text{CH}_2$ ), 136.67, 136.96, 137.48, 137.91 (phenyl-C).

### 3.2.6. Pentakis(trimethylsilylethyl)-*n*-propylbenzene (**3'**)

Reaction of 1.00 g (1.22 mmol) of **3** with 4 ml of 3 M of methylmagnesium chloride in THF (12.0 mmol) using the procedure described for **2'** gave a white powder (0.49 g, 65.0%), mp 169–170°C. Anal. Calc. for  $\text{C}_{34}\text{H}_{72}\text{Si}_5$ : C, 65.72; H, 11.68. Found: C, 65.9; H, 11.8.  $^1\text{H}$  NMR  $\delta$  0.09 (s, 27H,  $\text{CH}_3$ ), 0.10 (s, 18H,  $\text{CH}_3$ ), 0.75–0.81 (m, 10H,  $\text{CH}_2$ ), 1.05 (t,  $J = 7$  Hz, 3H,  $\text{CH}_3$ ), 1.52–1.58 (m, 2H,  $\text{CH}_2$ ), 2.42–2.45 (m, 2H,  $\text{CH}_2$ ), 2.46–2.56 (m, 10H,  $\text{CH}_2$ ).  $^{13}\text{C}$  NMR  $\delta$  -1.82, 1.61 ( $\text{CH}_3$ ), 14.97 ( $\text{CH}_3$ ), 19.56, 20.04, 20.13, 23.09, 23.17, 24.99, 31.90 ( $\text{CH}_2$ ), 135.34, 137.97, 138.27, 138.79 (phenyl-C).

### 3.2.7. Pentakis(dichloromethylsilylethyl)-*n*-butylbenzene (**4**)

Reaction of 0.86 g (6.40 mmol) of *n*-butylbenzene with 4.52 g (32.0 mmol) of dichloromethylvinylsilane and 0.47 g (3.52 mmol) of aluminum chloride using the procedure described for **1** gave 1.35 g (26.8%) of **4** as a white powder, mp 218–225°C.  $^1\text{H}$  NMR  $\delta$  0.87, (s, 15H,  $\text{CH}_3$ ), 1.01 (t,  $J = 7$  Hz, 3H,  $\text{CH}_3$ ), 1.32–1.38 (m, 10H,  $\text{CH}_2$ ), 1.49–1.54 (m, 2H,  $\text{CH}_2$ ), 2.48–2.52 (m, 2H,  $\text{CH}_2$ ), 2.71–2.79 (m, 12H,  $\text{CH}_2$ ,  $\text{CH}_2$ -Ar).  $^{13}\text{C}$  NMR  $\delta$  4.90, 4.98, 5.02 ( $\text{CH}_3$ ), 14.01 ( $\text{CH}_3$ ), 21.76, 22.02, 22.30, 23.52, 23.87, 24.05, 24.21, 24.38, 24.50, 29.41, 34.19 ( $\text{CH}_2$ ), 136.64, 136.98, 137.37, 137.55, 137.86 (phenyl-C).

### 3.2.8. Pentakis(trimethylsilylethyl)-*n*-butylbenzene (**4'**)

Reaction of 0.30 g (0.36 mmol) of **4** with 3 ml of 3 M of methylmagnesium chloride in THF (9.0 mmol) using the procedure described for **2'** gave **4'** as a white powder (0.19 g, 83.7%), mp 157–161°C. Anal. Calc. for  $\text{C}_{35}\text{H}_{74}\text{Si}_5$ : C, 66.16; H, 11.74. Found: C, 66.1; H, 11.9.  $^1\text{H}$  NMR  $\delta$  0.078 (s, 27H,  $\text{CH}_3$ ), 0.083 (s, 18H,  $\text{CH}_3$ ), 0.73–0.82 (m, 10H,  $\text{CH}_2$ ), 0.99 (t,  $J = 7$  Hz, 3H,  $\text{CH}_3$ ), 1.22–1.27 (m, 2H,  $\text{CH}_2$ ), 1.45–1.48 (m, 2H,  $\text{CH}_2$ ), 2.44–2.55 (m, 12H,  $\text{CH}_2$ ,  $\text{CH}_2$ -Ar).  $^{13}\text{C}$  NMR  $\delta$  -1.77, -1.68 ( $\text{CH}_3$ ), 13.96, 14.14 ( $\text{CH}_3$ ), 17.36, 19.55, 19.65, 19.86, 20.07, 20.14, 23.09, 23.16, 23.52, 23.74, 24.99, 29.30, 34.09 ( $\text{CH}_2$ ), 135.37, 137.97, 138.21, 138.75 (phenyl-C).

### 3.2.9. Tetrakis(dichloromethylsilylethyl)-*p*-xylene (**5**)

Reaction of 0.86 g (8.20 mmol) of *p*-xylene with 4.60 g (33.0 mmol) of dichloromethylvinylsilane and

0.22 g (1.65 mmol) of aluminum chloride using the procedure described for **1** gave 3.48 g (63.6%) of **5** as a white powder, mp 193–198°C. HRMS (m/e): Calc. for  $\text{C}_{20}\text{H}_{34}\text{Si}_4\text{Cl}_8$  ( $\text{M}^+$ ), 665.9246; Found, 665.9246.  $^1\text{H}$  NMR  $\delta$  0.88 (s, 12H,  $\text{CH}_3$ ), 1.28–1.34 (m, 8H,  $\text{CH}_2$ ), 2.29 (s, 6H,  $\text{CH}_3$ ), 2.80–2.85 (m, 8H,  $\text{CH}_2$ ).  $^{13}\text{C}$  NMR  $\delta$  5.11 ( $\text{CH}_3$ ), 15.26 ( $\text{CH}_2$ ), 22.71 ( $\text{CH}_3$ ,  $\text{CH}_2$ ), 131.54, 137.55 (phenyl-C).

### 3.2.10. Tetrakis(trimethylsilylethyl)-*p*-xylene (**5'**)

Reaction of 3.06 g (4.60 mmol) of **5** with 16 ml of 3 M of methylmagnesium chloride in THF (48.0 mmol) using the procedure described for **2'** gave **5'** as a white powder, which recrystallized from hexane to give colorless needles (1.15 g, 49.7%), mp 178–180°C. Anal. Calc. for  $\text{C}_{28}\text{H}_{58}\text{Si}^4$ : C, 66.32; H, 11.53. Found: C, 66.0; H, 11.7.  $^1\text{H}$  NMR  $\delta$  0.12 (s, 36H,  $\text{CH}_3$ ), 0.73–0.79 (m, 8H,  $\text{CH}_2$ ), 2.24 (s, 6H,  $\text{CH}_3$ ), 2.57–2.63 (m, 8H,  $\text{CH}_2$ ).  $^{13}\text{C}$  NMR  $\delta$  -1.79 ( $\text{CH}_3$ ), 15.11 ( $\text{CH}_2$ ), 18.58 ( $\text{CH}_2$ ), 23.95 ( $\text{CH}_3$ ), 130.50, 138.83 (phenyl-C).

### 3.2.11. Polyalkylation of mesitylene with dichloromethylvinylsilane

Dichloromethylvinylsilane (3.30 g, 23.4 mmol) was added dropwise to the stirred solution of mesitylene (0.86 g, 7.17 mmol) and aluminum chloride (0.12 g, 0.90 mmol) in 15 ml of dried hexane at room temperature. After the addition was completed, the reaction mixture stirred for 12 h at room temperature. White solids, precipitated from the hexane solution, was filtered and dissolved in 10 ml of dried THF and filtered off upon cooling ( $-10^\circ\text{C}$ ). Evaporation of THF-filtrate and hexane-filtrate on 2/3 of volume yields 1.43 g (38.0%) of 2,4,6-Tris(dichloromethylsilylethyl)mesitylene (**6**) as a white solid. Further recrystallization from hexane gave long-needles, mp 141–142°C. HRMS (m/e): Calc. for  $\text{C}_{18}\text{H}_{30}\text{Si}_3\text{Cl}_6$  ( $\text{M}^+$ ), 539.9787; Found, 539.9786.  $^1\text{H}$  NMR  $\delta$  0.88 (s, 9H,  $\text{CH}_3$ ), 1.27–1.33 (m, 6H,  $\text{CH}_2$ ), 2.31 (s, 9H,  $\text{CH}_3$ ), 2.85–2.91 (m, 6H,  $\text{CH}_2$ ).  $^{13}\text{C}$  NMR  $\delta$  5.11 ( $\text{CH}_3$ ), 15.49 ( $\text{CH}_2$ ), 21.62 ( $\text{CH}_3$ ), 23.08 ( $\text{CH}_2$ ), 131.18, 138.17 (phenyl-C). Further evaporation of hexane filtrate yields second portion of 2,4-bis(dichloromethylsilylethyl)mesitylene (**6-1**) as white solids (1.54 g, 37%), mp 90–91°C.  $^1\text{H}$  NMR  $\delta$  0.88 (s, 6H,  $\text{CH}_3$ ), 1.27–1.32 (m, 4H,  $\text{CH}_2$ ), 2.31 (s, 9H,  $\text{CH}_3$ ), 2.81–2.87 (m, 4H,  $\text{CH}_2$ ), 6.89 (s, 1H, phenyl-H).  $^{13}\text{C}$  NMR  $\delta$  5.07 ( $\text{CH}_3$ ), 14.93 ( $\text{CH}_2$ ), 19.67, 21.47 ( $\text{CH}_3$ ), 22.46 ( $\text{CH}_2$ ), 130.45, 133.09, 133.25, 137.85 (phenyl-C). Vacuum distillation of residue after separation of **6-1** yields 0.13 g (7.0%) of (dichloromethylsilylethyl)mesitylene (**6-2**) as colorless liquids, bp 94–96°C/1 Torr, solidified upon standing, mp 40–42°C.  $^1\text{H}$  NMR  $\delta$  0.96 (s, 3H,  $\text{CH}_3$ ), 1.36–1.41 (m, 2H,  $\text{CH}_2$ ), 2.38 (s, 3H,  $\text{CH}_3$ ), 2.41 (s, 6H,  $\text{CH}_3$ ), 2.87–2.92 (m, 2H,  $\text{CH}_2$ ), 6.96 (s, 2H, phenyl-H).  $^{13}\text{C}$  NMR  $\delta$  5.12 ( $\text{CH}_3$ ), 19.61 ( $\text{CH}_2$ ), 20.95, 21.40 ( $\text{CH}_3$ ), 21.83 ( $\text{CH}_2$ ), 129.27, 135.49, 136.67 (phenyl-C).

Methylations of corresponding chloro-derivatives **6**, **6-1**, and **6-2** using methylmagnesium chloride described for **1'** were proceeded. 2,4,6-tris(trimethylsilylethyl)mesitylene (**6'**) was purified by recrystallization from EtOH as white solids in 73.0% yield, mp 104–105°C. <sup>1</sup>H NMR δ 0.10 (s, 27H, CH<sub>3</sub>), 0.68–0.76 (m, 6H, CH<sub>2</sub>), 2.24 (s, 9H, CH<sub>3</sub>), 2.59–2.63 (m, 6H, CH<sub>2</sub>). <sup>13</sup>C NMR δ -1.78 (CH<sub>3</sub>), 15.22 (CH<sub>2</sub>), 17.10 (CH<sub>3</sub>), 24.48 (CH<sub>2</sub>), 129.86, 140.27 (phenyl-C). 2,4-Bis(trimethylsilylethyl)mesitylene (**6'-1**) and (trimethylsilylethyl)mesitylene (**6'-2**) were purified by vacuum distillation as colorless viscous liquids, respectively. 2,4-Bis(trimethylsilylethyl)mesitylene (**6'-1**); yield 77%, bp 124–126°C/1 Torr. <sup>1</sup>H NMR δ 0.09 (s, 18H, CH<sub>3</sub>), 0.68–0.71 (m, 4H, CH<sub>2</sub>), 2.24 (s, 3H, CH<sub>3</sub>), 2.25 (s, 6H, CH<sub>3</sub>), 2.54–2.60 (m, 4H, CH<sub>2</sub>), 6.82 (s, 1H, phenyl-H). <sup>13</sup>C NMR δ -1.76 (CH<sub>3</sub>), 14.73 (CH<sub>2</sub>), 16.96, 19.68 (CH<sub>3</sub>), 23.94 (CH<sub>2</sub>), 130.14, 132.16, 132.55, 140.32 (phenyl-C). (Trimethylsilylethyl)mesitylene (**6'-2**); yield 77.0%, bp 78°C/1 Torr. <sup>1</sup>H NMR δ 0.24 (s, 9H, CH<sub>3</sub>), 0.80–0.86 (m, 2H, CH<sub>2</sub>), 2.40 (s, 3H, CH<sub>3</sub>), 2.42 (s, 6H, CH<sub>3</sub>), 2.67–2.73 (m, 2H, CH<sub>2</sub>), 6.97 (s, 2H, phenyl-H). <sup>13</sup>C NMR δ -1.74 (CH<sub>3</sub>), 16.78 (CH<sub>2</sub>), 19.58, 20.95 (CH<sub>3</sub>), 23.27 (CH<sub>2</sub>), 129.08, 134.62, 135.20, 139.36 (phenyl-C).

### 3.2.12. 2,4,6-tris(methylsilylethyl)mesitylene (**6**)

To a suspension of 1.00 g (26.3 mmol) of lithium aluminum hydride in 50 ml of dried THF, 5.00 g (9.21 mmol) of **6** in 80 ml of THF solution was added dropwise with stirring. The resulting mixture was stirred for 2 h and hydrolyzed. The organic layer was extracted with diethyl ether, washed with water, and dried over anhydrous MgSO<sub>4</sub>. Evaporation of solvent left yellow oils, which was dissolved in 1 ml of hexane and subject to column chromatography (silica gel, hexane) to give **6''** as a white powder (2.25 g, 73.0%), mp 50–51°C. Anal. Calc. for C<sub>18</sub>H<sub>36</sub>Si<sub>3</sub>: C, 64.2; H, 10.78. Found: C, 64.40; H, 11.0. <sup>1</sup>H NMR δ 0.31 (t, *J* = 4 Hz, 9H, CH<sub>3</sub>), 0.94–1.00 (m, 6H, CH<sub>2</sub>), 2.34 (s, 9H, CH<sub>3</sub>), 2.76–2.82 (m, 6H, CH<sub>2</sub>), 3.89–3.94 (m, 6H, Si-H). <sup>13</sup>C NMR δ -8.50 (CH<sub>3</sub>), 10.97 (CH<sub>2</sub>), 15.48 (CH<sub>3</sub>), 25.88 (CH<sub>2</sub>), 130.49, 139.75 (phenyl-C).

### 3.3. X-Ray crystallographic studies

The X-ray crystallographic data were collected on a Siemens P4/DCC using Mo K $\alpha$  radiation ( $\lambda$  = 0.71073 Å) with a graphite monochromator. The structures were solved using direct methods and refined by full-matrix least-squares on *F*<sup>2</sup> using SHELXTL PLUS 5.0 (PC) software package [37]. All non-hydrogen atoms were refined with anisotropic thermal parameters in the later stages of refinement. All hydrogen atoms except those of methyl groups were placed in idealized posi-

tions and refined using the riding model with general isotopic temperature factors. Details of the crystal data and a summary of intensity data collection parameters and bond lengths and angles are given in Tables 3 and 4.

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